

# Magnetic field induced quantum phase transition of the $S = 1/2$ antiferromagnet $\text{K}_2\text{NaCrO}_8$

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The magnetic properties of alkali-metal peroxychromate  $\text{K}_2\text{NaCrO}_8$  are governed by the  $S = 1/2$  pentavalent chromium cation,  $\text{Cr}^{5+}$ . Specific heat, magnetocalorimetry, ac magnetic susceptibility, torque magnetometry, and inelastic neutron scattering data have been acquired over a wide range of temperature, down to 60 mK, and magnetic field, up to 18 T. The magnetic interactions are quasi-two-dimensional prior to long-range ordering, where  $T_N = 1.66$  K in  $H = 0$ . In the  $T \rightarrow 0$  limit, the magnetic field tuned antiferromagnetic-ferromagnetic phase transition suggests a critical field  $H_c = 7.270$  T and a critical exponent  $\alpha = 0.481 \pm 0.004$ . The neutron data indicate the magnetic interactions may extend over intra-planar nearest-neighbors and inter-planar next-nearest-neighbor spins.

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The study of the similarities and differences between classical and quantum phase transitions has a rich history, and recent research has focused on systems in reduced dimensions.<sup>1,2,3,4</sup> For magnetic systems, the model Hamiltonian is often written as

$$\mathcal{H} = \sum_{(i,j)} J_{ij} \vec{S}_i \cdot \vec{S}_j + \vec{H} \cdot \vec{g} \cdot \sum_i \vec{S}_i, \quad (1)$$

where the first sum over  $(i,j)$  is often restricted to nearest-neighbors ( $nn$ ) but may sometimes extend to include next-nearest neighbors ( $nnn$ ),  $J > 0$  indicates antiferromagnetic interactions, and the Zeeman (second) term includes the presence of the externally applied magnetic field  $H$  and an anisotropic Landé  $g$ -tensor. It is important to emphasize that both the spin and spatial dimensions are crucial elements of any model, and in this context, the critical exponents can be considered fingerprints for classifying the nature of the transition. In particular, the order parameter describing the transition can be characterized by  $(T_c - T)^\beta$  as the temperature  $T$  approaches the critical temperature  $T_c$  or, in the  $T \rightarrow 0$  limit, by  $(H_c - H)^\alpha$  for a quantum phase transition tuned by the magnetic field.<sup>1,2,3,4,5,6,7,8,9,10,11</sup>

The purpose of the present work was to consider the curious case of the pentavalent chromium cation,  $\text{Cr}^{5+}$ , an  $S = 1/2$  ( $3d^1$ ) ion that is not a common choice for condensed matter research.<sup>12,13,14,15,16,17,18,19,20</sup> Specifically, the alkali-metal peroxychromate  $\text{K}_2\text{NaCrO}_8$  crystallizes with orthorhombic symmetry (space group  $Pbcm$ ) with the lattice parameters  $a = 8.5883$  Å,  $b = 7.9825$  Å, and  $c = 9.2432$  Å at 173 K.<sup>14</sup> The  $\text{Cr}^{5+}$  ion is bonded to four peroxy ( $\text{O}_2$ )<sup>2-</sup> ligands in a dodecahedral geometry, and the ions form the three dimensional network shown in Fig. 1.<sup>14,18</sup> The data from EPR studies showed the  $g$ -tensor is anisotropic, with  $g_z = 1.9851$ ,  $g_y = 1.9696$ ,

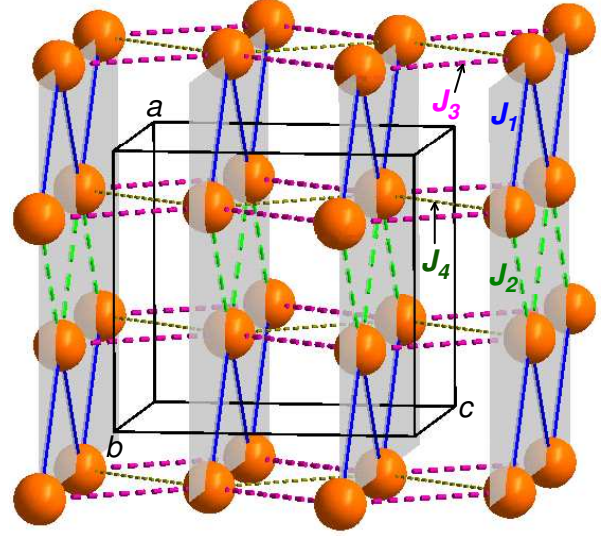


FIG. 1: (Color online) Spin network in  $\text{K}_2\text{NaCrO}_8$  as seen along the  $b$ -axis, where only the  $\text{Cr}^{5+}$  ions are shown for clarity. The vertical planes are the mirror planes containing  $J_1$  (solid lines) and the  $J_2$  (dashed lines) paths connecting the  $nn$   $\text{Cr}^{5+}$  ions. Exchange paths corresponding to  $nnn$  interactions are labeled as  $J_3$  (short-dashed lines) and  $J_4$  (dotted lines).

and  $g_x = 1.9636$ , the electronic ground state is  $d_{z^2}$ , and the magnetic  $z$ -axis is along the  $[110]$  crystal direction. During studies of the static magnetic susceptibility,  $\chi_{dc}(H = 0.3 \text{ T}, 1.8 \text{ K} \leq T \leq 20 \text{ K})$ , and the specific heat,  $C(0 \leq H \leq 9 \text{ T}, 1.8 \text{ K} \leq T \leq 10 \text{ K})$ , Cage and Dalal<sup>14</sup> observed ordering signatures in poly-

crystalline samples. More specifically, while a rounded maximum was observed in  $\chi_{dc}(H = 0.3 \text{ T}, T \approx 2.29 \text{ K})$ , the  $C(H \approx 0, T \approx 1.8 \text{ K})$  data appeared to possess a  $\lambda$ -like peak. These signatures indicate the presence of low dimensional antiferromagnetic behavior and the onset of long-range antiferromagnetic ordering. More recently, Choi *et al.*<sup>18</sup> performed low temperature magnetization and  $^{23}\text{Na}$  NMR measurements and identified a quantum phase transition from an antiferromagnetically ordered state to a ferromagnetically polarized state at critical field  $H_c$  of about 7.4 T, with  $\beta = 0.44 \pm 0.05$  in  $H = 5 \text{ T}$  and  $\beta = 0.53 \pm 0.05$  in  $H = 6.8 \text{ T}$ . Since mean-field theory yields  $\beta = 1/2$  for magnetization, these workers concluded that the high field magnetization of  $\text{K}_2\text{NaCrO}_8$  is mean-field-like.

Herein, the results of specific heat, magnetocaloric effect, ac magnetic susceptibility, and torque magnetometry are reported to construct the magnetic phase diagram of  $\text{K}_2\text{NaCrO}_8$ , with particular emphasis on the  $T \rightarrow 0$  limit of the magnetic field induced quantum phase transition. The data indicate the magnetic interactions are quasi-two-dimensional prior to long-range ordering. Inelastic neutron scattering studies in zero magnetic field confirm the antiferromagnetic transition occurs without any low temperature structural transitions and suggest the strongest magnetic interactions may include both  $nn$  and  $nnn$  ions. Furthermore, in the critical regime, the specific heat and magnetocaloric effect systematically identify the phase transition, while the magnetic measurements, although consistent with each other, yield a slightly shifted trend as  $T \rightarrow 0$ .

Single crystals of  $\text{K}_2\text{NaCrO}_8$  were prepared by modification of the method of Riesenfeld.<sup>12</sup> The synthesis involves the reduction of  $\text{Cr}^{6+}$  by 30%  $\text{H}_2\text{O}_2$  at  $5^\circ\text{C}$  in the 1:1 molar mixture of aqueous  $\text{NaOH}$  and  $\text{KOH}$ . Specific heat and magnetocaloric data were collected on single crystals with  $H$  applied along the  $c$ -axis. The specific heat studies employed the relaxation technique,  $150 \text{ mK} \leq T \leq 20 \text{ K}$ , with  $H \leq 18 \text{ T}$  using two different instruments. The magnetic specific heat,  $C_{\text{mag}}$ , was obtained by subtracting the zero-field Debye contribution, namely  $C_{\text{phonon}} = (1.85 \times 10^{-3}) T^3 \text{ J}/(\text{mol K}^4)$ , from the total specific heat at all fields, and was integrated to yield the magnetic entropy,  $S_{\text{mag}}(T)$ , Fig. 2. The magnetocaloric data,  $150 \text{ mK} \leq T \leq 600 \text{ mK}$ , were collected in  $H \leq 18 \text{ T}$  with a field sweep rate of  $0.2 \text{ T}/\text{min}$ , Fig. 3a. For the ac susceptibility,  $\chi_{ac}$ , a sample consisting of a random arrangement of microcrystallites (8.44 mg) was mounted, using GE varnish dissolved in ethanol, on a silver strip and wrapped in Kapton tape. The measurements were performed in a homemade dilution refrigerator probe using a standard set of inductively coupled coils operating at  $1.114 \text{ kHz}$ , Fig. 3b. Torque magnetometry, performed down to  $280 \text{ mK}$  and up to  $18 \text{ T}$ , utilized a single crystal sample (1.2 mg) mounted using Stycast epoxy on a 0.005 inch thick CuBe cantilever soldered to a post. The torque experienced by the sample deflects the cantilever, and the deflection was measured capacitively through a

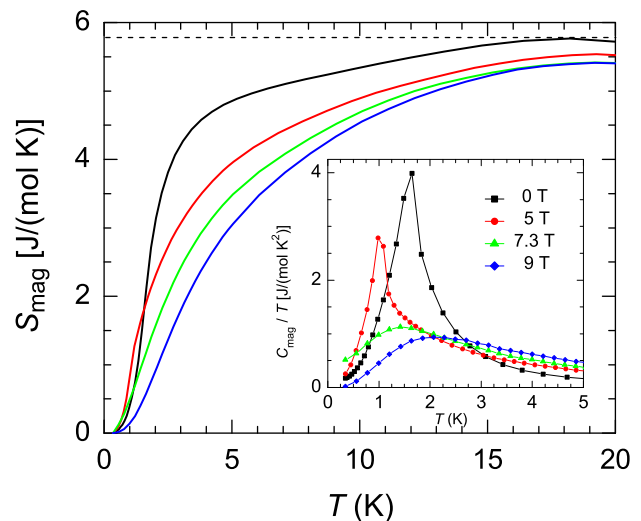


FIG. 2: (Color online) The temperature dependence of the magnetic entropy,  $S_{\text{mag}}(T)$ , at several representative magnetic fields. The inset shows the temperature dependence of the magnetic specific heat divided by temperature,  $C_{\text{mag}}(T)/T$ , at the same magnetic fields.  $C_{\text{mag}}(T)$  was obtained by subtracting a lattice contribution from the total specific heat, see text.  $S_{\text{mag}}(T)$  was obtained by integrating the data shown in the inset. As  $T$  increases,  $S_{\text{mag}}(T)$  slowly approaches the  $R \ln 2$  value, designated by the dashed line, as expected for a  $S = 1/2$  system. In  $H = 0$ , about 60% of the entropy is acquired above  $T_N$ , indicating significant contributions from short range correlations.

manual capacitance bridge excited at  $30 \text{ V}$  and  $5 \text{ kHz}$ , Fig. 3c. Zero field neutron scattering work down to  $1.4 \text{ K}$  used a powder-like sample, generated by grinding microcrystals, that was mounted on the NIST-CNS disk chopper spectrometer (DCS) tuned to a wavelength of  $4.8 \text{ \AA}$ .

The distinct  $\lambda$  anomaly observed in the magnetic specific heat (Fig. 2) at  $T_N = 1.66 \text{ K}$  and  $H = 0$  indicates that  $\text{K}_2\text{NaCrO}_8$  undergoes long-range antiferromagnetic ordering (LRAFO) as conjectured from earlier specific heat measurements.<sup>14</sup> The LRAFO is suppressed in the presence of a magnetic field, as  $T_N$  shifts slowly to lower temperatures until  $H$  reaches about  $5 \text{ T}$  and rapidly thereafter until the LRAFO is completely suppressed around  $7.3 \text{ T}$ . For  $H > 5 \text{ T}$ , the Schottky-type anomaly overlapping the LRAFO at zero field becomes the dominant feature of  $C_{\text{mag}}(T)$ , and the corresponding position in temperature of the heat capacity maximum shifts to higher temperatures. Consequently, the position of the phase transition is harder to identify. On the other hand, the magnetocaloric effect produces peaks in the up and down sweep directions, and these features correspond to the magnetic phase transition, while the center of these anomalies is identified as the transition point, Fig. 3. In Fig. 4, the transition points identified by these two methods are shown to yield a single trend of the phase boundary between the LRAFO and the polarized ferromagnetic state.

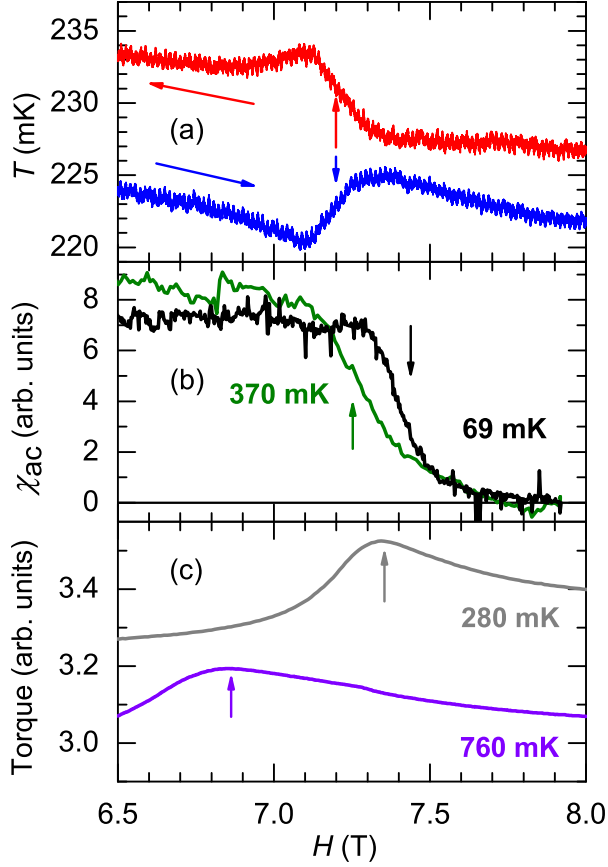


FIG. 3: (Color online) (a) The magnetocaloric effect curves for up and down field sweeps near 230 mK. (b) The ac susceptibility,  $\chi_{ac}(H)$  at 69 mK and 370 mK. (c) The isothermal magnetic torque measured as a function of  $H$ . In each panel, the arrows designate the positions taken as the field induced phase transition.

With respect to the magnetic studies using  $\chi_{ac}$  and torque, the signatures designating the critical field of the transition are sharpest as  $T \rightarrow 0$ . For  $\chi_{ac}$ , the inflection point between the low and high field regions is often used, Fig. 3b. Alternatively, these data are integrated to yield the isothermal field dependence of the magnetization,  $M(H)$ , but an extrapolation protocol must be used as the location of the critical field is often smeared.<sup>21,22,23</sup> In our case, both routines provide essentially the same results that are plotted in Fig. 4. For the torque measurement, the peak of the response appears on a smooth, nearly quadratic background, Fig. 3c, and is taken as the location of the transition, Fig. 4. It is interesting to note that both techniques indicate a phase boundary that is slightly shifted from the one given by the specific heat and magnetocaloric effect results, Fig. 4.

Since the response of the specific heat unambiguously marks the transition and the magnetocaloric effect data

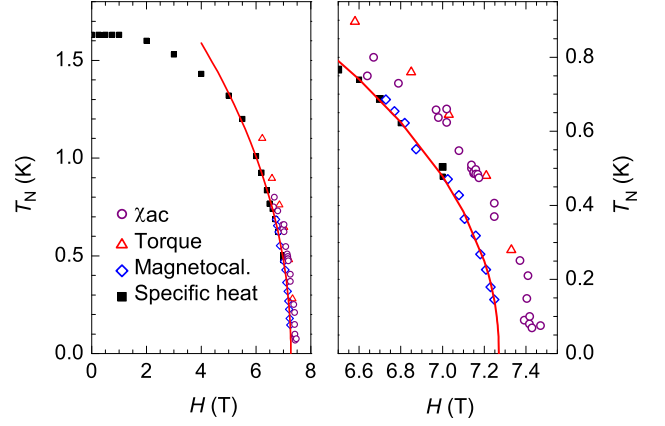


FIG. 4: (Color online) Magnetic phase diagram of  $K_2NaCrO_8$ . The solid line corresponds to Eq. 2 with  $H_c = 7.27$  T and  $\alpha = 0.481 \pm 0.004$ . The right panel provides an expanded view near  $H_c$  ( $T \rightarrow 0$ ), where the specific heat and magnetocaloric transition points are systematically different than the ones extracted from standard analysis of the magnetic measurements,  $\chi_{ac}$  and torque.

identify the same critical field, these results were used to fit to

$$T_N = A(H_c - H)^\alpha \quad (2)$$

Care must be used when fitting Eq. 2, as both  $H_c$  and  $\alpha$  must be resolved.<sup>7,8,9,10,11</sup> Consequently, the “ $T$ -window” analysis and empirical convergence methods<sup>8</sup> were employed, by systematically varying the maximum temperature of the fits from 1 K to 230 mK, to extract the values of  $H_c = 7.27$  T and  $\alpha = 0.481 \pm 0.004$ . In detail, to extract  $H_c$ , the low temperature ( $T < 1$  K) phase boundary was fit to Eq. 2 for various  $\alpha$  values in a temperature window,  $T_W$ , of decreasing size. For example, the phase boundary with a window size of 20 data points was fit to Eq. 2 with  $H_c$  and  $A$  as fitting parameters, while holding  $\alpha = 0.48$ . Then the window was successively reduced by removing the highest temperature point, and the fitting procedure was repeated. The resulting  $H_c$  values can then be plotted as a function of the upper limit of  $T_W$ , Fig. 5. The whole fitting procedure is then repeated for various fixed  $\alpha$  values. The value of  $H_c = 7.2696 \pm 0.0002$  T was then obtained by taking a weighted average of the linearly extrapolated  $H_c(T_W \rightarrow 0)$  values corresponding to various  $\alpha$  values. This convergence of  $H_c$  to a single value allows a more precise determination of  $\alpha$  than possible with a three parameter fit in which  $H_c$ ,  $\alpha$ , and  $A$  are simultaneous fitting parameters. The critical exponent  $\alpha$  is then determined by following the same procedure, where the  $T$ -window analysis is performed when fixing  $H_c = 7.2696$  T, Fig. 5, and the result is  $\alpha = 0.481 \pm 0.004$ . Establishing the critical exponent of the transition begs the questions about the details of the network of magnetic interactions, so inelastic neutron scattering experiments were performed.

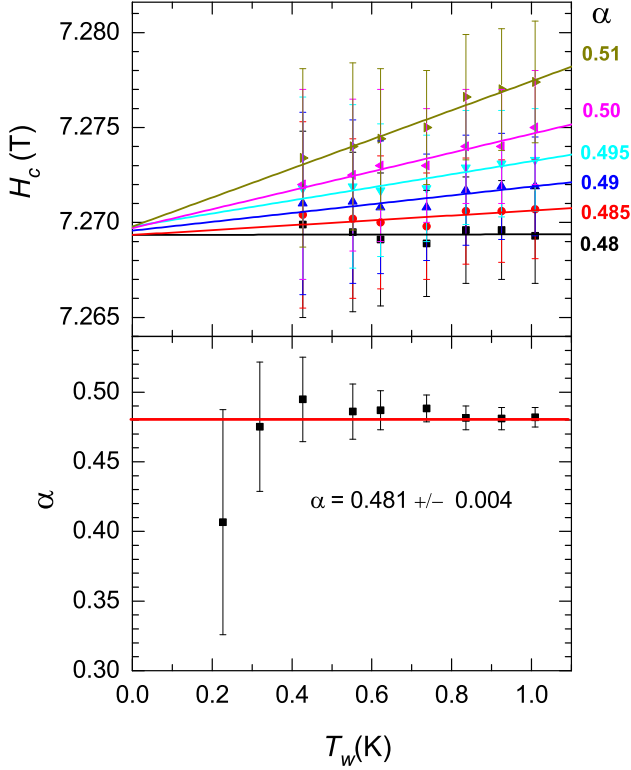


FIG. 5: (Color online) Estimates of (top panel) the critical field  $H_c$  and (bottom panel) the critical exponent  $\alpha$  obtained from the “ $T$ -window” analysis of the transition, see text for detailed description. The results are  $H_c = 7.2696 \pm 0.0002$  T and  $\alpha = 0.481 \pm 0.004$ .

The neutron scattering pattern at 1.725 K (Fig. 6a) reveals a magnetic excitation above  $\Delta E = 0.2$  meV. After decreasing the temperature to 1.7 K (Fig. 6b), this excitation becomes sharper with a well-defined mode near  $\Delta E = 0.5$  meV. When the magnetic excitations are summed over all  $Q$ , the broad peak near  $\Delta E = 0.5$  meV sharpens for  $T < 1.725$  K. The temperature dependence of the integrated area of the peak is consistent with the LRAFO observed in the zero-field specific heat.

Another noteworthy feature is that the excitation below the transition shows clear  $Q$  dependence, which has higher intensity at low  $Q$ . This magnetic contribution is consistent with an expression used to model the scattering from powders, where short-range, isotropic spin correlations persist to the first few coordination shells of neighboring spins,<sup>24</sup> namely

$$I(Q) \sim \sum_{i,j} \langle s_i s_j \rangle \frac{\sin(Q r_{i,j})}{Q r_{i,j}} \sim \frac{\sin(Q R)}{Q R}, \quad (3)$$

where the final result is for the case of spins correlated over the nearest neighbors. Consequently, only one value  $R$  of  $r_{ij}$  (the distance between spins at sites  $i$  and  $j$ ) is employed in our fitting procedure, where Eq. 3, multiplied by the magnetic form factor of the  $\text{Cr}^{5+}$  ion, has been

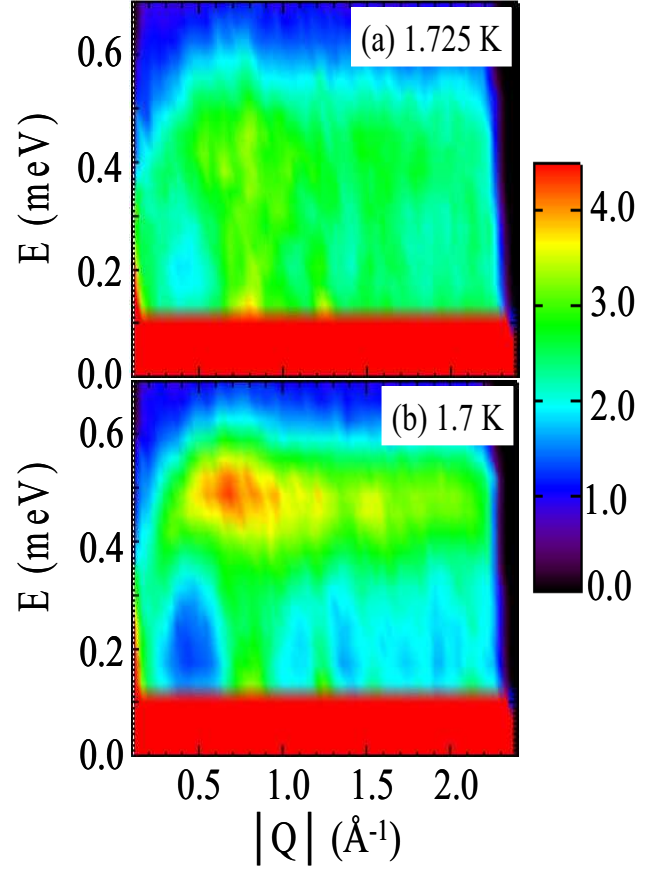


FIG. 6: (Color online) Inelastic neutron scattering spectra at (a) 1.725 K and (b) 1.7 K.

used to fit to the net intensity shown in Fig. 7a. This analysis yields  $R = 6$   $\text{\AA}$ , which is close to the  $nn$  and  $nnn$   $\text{Cr} \cdots \text{Cr}$  distances that are in the range 5.8 – 6.2  $\text{\AA}$ . Ergo, the magnetic correlations are short range, extending over  $nn$  and  $nnn$  neighbors, Fig. 1. Furthermore, with decreasing temperature, the lattice Bragg peaks do not show obvious splitting or intensity change, thereby excluding the possibility of a structural change. On the other hand, new magnetic Bragg peaks with low intensity develop below 1.725 K (Fig. 7b) and are consistent with the ordering of a small moment at  $T_N \approx 1.7$  K.

Equipped with the result that short range magnetic interactions appear to extend over  $nn$  and  $nnn$  ions, the underlying network of these interactions can be reexamined. Previous theoretical and experimental studies established that although most of the unpaired electron density is on the  $\text{Cr}^{5+}$  ion, a significant portion of it can be found on the bound  $(\text{O}_2)^{2-}$  ions.<sup>25,26,27,28</sup> Consequently, the potential superexchange pathways between  $\text{Cr}^{5+}$  ions in  $\text{K}_2\text{NaCrO}_8$  can be expected to involve the  $(\text{O}_2)^{2-}$ ,  $\text{Na}^+$  and  $\text{K}^+$  ions. Since the bond angle is an important factor in determining the ferromagnetic versus antiferromagnetic nature of the interactions,<sup>29,30,31</sup> the paths with larger  $\text{O} \cdots \text{Na/K} \cdots \text{O}$  angle are selected when more than



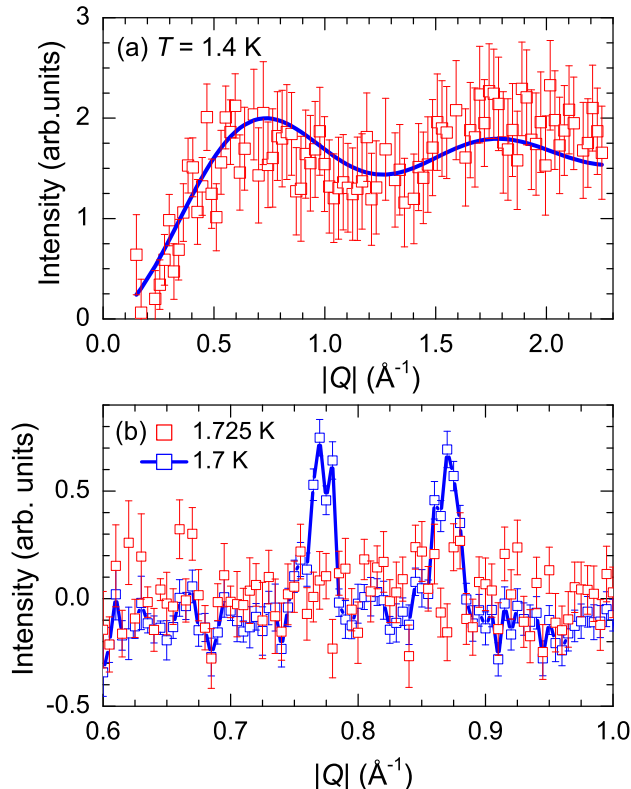


FIG. 7: (Color online) (a) A cut of the magnetic excitation near  $\Delta E = 0.5$  meV at  $T = 1.4$  K. The  $Q$  dependence of the intensity (open squares) is fit to Eq. 3 (solid line). (b) Appearance of the magnetic peaks at 1.7 K, after the data at 2 K have been subtracted as the lattice standard.

one possible exchange pathway for a given  $\text{Cr}^{5+} \dots \text{Cr}^{5+}$  distance are present. This analysis leads to the results given in Table I, which tabulates the most influential exchange interactions between  $nn$  (the intra-planar  $J_1$  and  $J_2$ )<sup>18</sup> and  $nnn$  (the inter-planar  $J_3$  and  $J_4$ )  $\text{Cr}^{5+}$  ions, Fig. 1. While the  $J_1$  path involves  $\text{Na}^+$  ions with a  $\text{Na} \dots \text{O}$  distance of  $\sim 2.4$   $\text{\AA}$  and a bond angle  $\angle \text{ONaO}$  of  $142^\circ$ , the  $J_2$  path involves  $\text{K}^+$  ions with  $\text{K} \dots \text{O}$  distance of  $\sim 3.0$   $\text{\AA}$  and an angle  $\angle \text{OKO}$  of  $166^\circ$ . The  $J_3$  path involves  $\text{Na}^+$  ions with a  $\text{Na} \dots \text{O}$  distance of  $\sim 2.4$   $\text{\AA}$  and a bond angle  $\angle \text{ONaO}$  of  $166^\circ$  and the  $J_4$  path involves  $\text{K}^+$  ions with a  $\text{K} \dots \text{O}$  distance of  $\sim 2.6$   $\text{\AA}$  and a bond angle  $\angle \text{OKO}$  of  $131^\circ$ . All of the data suggest the intra-layer interactions are somewhat stronger than the inter-layer ones, since the two-dimensional correlations develop before three-dimensional long-range order appears. Assuming a square lattice model, the intra-planar exchange interaction,  $J_{\text{intra}} \equiv (J_1 + J_2)/2$ , can be estimated

from the data. For example, fitting  $C_{\text{mag}}(T, H = 18 \text{ T})$  yields  $J_{\text{intra}} \sim 2.1$  K, whereas  $H_c = 4J_{\text{intra}}/g\mu_B$ , gives  $J_{\text{intra}} \sim 2.4$  K. Both of these estimates are close to the value of 2.44 K obtained by fitting  $\chi_{\text{dc}}(T)$  using a two-dimensional high temperature series expansion.<sup>14</sup>

In summary, the low temperature, high magnetic field phase diagram of  $\text{K}_2\text{NaCrO}_8$  has been established. In the  $T \rightarrow 0$  limit, the magnetic field tuned antiferromagnetic-ferromagnetic phase transition suggests a critical field  $H_c = 7.270$  T and a critical exponent  $\alpha = 0.481 \pm 0.004$ . The value of this critical exponent, Eq. 2, depends on the universality class of the quantum phase transition, where  $\alpha = 2/3$  is expected for Bose-Einstein condensation (BEC)<sup>1,2,3,4</sup> and  $\alpha = 1/2$  is predicted for Ising-like spins.<sup>2,10,32</sup> The present data do not allow us to unambiguously differentiate between these two possible descriptions, since a broad range of exponents is expected if the transition is not probed at sufficiently low temperatures.<sup>7</sup> The neutron data suggest the magnetic interactions extend over intra-planar nearest-neighbors and inter-planar next-nearest-neighbor spins. For a deeper understanding of these results, especially the value of the critical exponent, inelastic neutron scattering experiments should be performed on single crystals that are cooled to millikelvin temperatures in the presence of the magnetic field capable of spanning  $H_c$ . Fluctuation-induced heat release<sup>33</sup> and NMR<sup>34</sup> studies are alternatives that might provide decisive information.

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TABLE I: Possible magnetic exchange pathways between  $\text{Cr}^{5+}$  in  $\text{K}_2\text{NaCrO}_8$ . The labels for the atoms is the same as used by Cage and Dalal<sup>14</sup> and the  $J_1$  and  $J_2$  designations are the same as used by Choi *et al.*<sup>18</sup>

Label	$\text{Cr} \dots \text{Cr}$ ( $\text{\AA}$ )	Pathway
$J_1$	5.837	$\text{O1} \dots \text{Na2} \dots \text{O2}$
$J_2$	5.888	$\text{O2} \dots \text{K1} \dots \text{O2}$
$J_3$	5.974	$\text{O6} \dots \text{Na2} \dots \text{O6}$
$J_4$	6.243	$\text{O3} \dots \text{K1} \dots \text{O3}$

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